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(54) Conductive adhesive and connection structure using the same

Leitfähiger Klebstoff und diesen verwendende Verbindungsanordnung Adhésif conducteur et structure de connexion l'utilisant

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(56) References cited: **DE-A- 19 732 664** 

- DATABASE WPI Section Ch, Week 199330
   Derwent Publications Ltd., London, GB; Class A85, AN 1993-237618 XP002176413 & JP 05 159622 A (SEKISUI FINE CHEM CO LTD), 25 June 1993 (1993-06-25)
- DATABASE WPI Section Ch, Week 199427
   Derwent Publications Ltd., London, GB; Class A21, AN 1994-222159 XP002176628 & JP 06 157876 A (AJINOMOTO KK), 7 June 1994 (1994-06-07)

#### Description

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[0001] The present invention relates to a conductive adhesive used for solder-free mounting of electronic components and a structure connected by using the same.

[0002] In recent years, due to the increased environmental consciousness, the electrical industry now faces the movement to abolish totally lead-containing solder used for mounting of electronic components, and this movement is becoming significant.

[0003] As for lead-free mounting techniques, mounting techniques using lead-free solder have been developed keenly and a part of the development has come into practical use. However, still a number of problems remains to be solved, such as influence of a high mounting temperature on low heat-resistant components or lead-free electrodes.

[0004] On the other hand, only a few examples of lead-free mounting with the use of a conductive adhesive has been reported so far, which has the following advantages besides the aspect of lead-free mounting.

[0005] First, the processing temperature of around 150°C is lower than the temperature for soldering, and electronic components with higher performance can be realized with low cost. Secondly, the specific gravity of a conductive adhesive is about half that of solder, so that electronic equipment can be lightened more easily. Thirdly, since the connection is not achieved by means of metal as in soldering, metal fatigue does not occur, and the reliability of mounting is excellent.

[0006] Therefore, it is expected that a revolutionary mounting process that fulfills the needs of environment, low cost, and high reliability can be realized by completing the mounting technique using a conductive adhesive.

[0007] The problem with the use of a conductive adhesive for mounting is that the adhesive strength is lower than that of solder. In particular, the strength against bending stress is about 1/10 of that of solder, so that an electronic component with a large area to which bending stress easily is applied sometimes suffers from the separation of the electrode with the conductive adhesive at the interface, thereby causing connection failures.

[0008] Numerous attempts to improve the adhesive strength have been reported, but not even one technique is capable of achieving the same strength as that of solder. One representative example will be shown below.

[0009] As described in the publication supervised by Hiroo Miyairi, "Development of Functional Adhesives and the New Technology" (edited by CMC, June 30, 1997, 194 pages), for example, a number of techniques to improve the adhesive strength by adding an organic metal called a silane coupling agent into the adhesive material, which can form a chemical bond with both resin and metal, has been reported.

[0010] However, the aforementioned techniques utilize either a dehydration reaction or a substitution reaction, so that the reactivity of the coupling agent with resin or with metal was poor, and the conditions (temperature, concentration of hydrogen ion, etc.) for optimizing the reaction could not be determined clearly, and so forth. Therefore, a considerable improvement of the adhesive strength was difficult to be achieved.

[0011] Furthermore, JP9(1997)-176285A proposes the use of a resin with a phosphoric ester group introduced into the skeleton as a binder resin. According to this method, the functional group in the binder resin is adsorbed to the metal, so that some improvement of the adhesive strength can be achieved. However, the adsorptive power is poor in comparison with a covalent bond or a coordinate bond, so that considerably improved effects could not be obtained.

[0012] As described above, the improvement of the adhesive strength has been the key factor to make the practical use of the mounting technique using a conductive adhesive.

[0013] It is an object of the present invention to solve the conventional problems described above by providing a conductive adhesive having considerably improved adhesive strength and higher reliability against bending stress. Another object of the present invention is to provide a structure connected by using this conductive adhesive.

[0014] To achieve the above object, a conductive adhesive of the present invention includes a binder resin and a metal filler as main components, wherein the binder resin contains a functional group in its molecular chain that forms a multidentate bonding with an electrode metal after the binder resin is adhered and wherein taking the conductive adhesive as 100 wt%, the binder resin is contained in an amount between 5 and 25 wt%, and the metal filler is contained in an amount between 75 and 95 wt%.

[0015] A connection structure of the present invention is formed by using a conductive adhesive to connect the adhesive with an electrode electrically, wherein the conductive adhesive includes a binder resin and a metal filler as main components, and the binder resin contains a functional group in its molecular chain that forms a multidentate bonding with an electrode metal after the binder resin is adhered.

[0016] In the present invention, the multidentate bonding refers to a state in which multidentate ligands (a plurality of chelating ligands) introduced into the binder resin form coordinate bonds with the electrode metal. In other words, the adhesion is not achieved only by using the ordinary weak van der Waal's power by hydrogen bonding, but instead, a chemical bond (coordinate bond) is formed between the binder resin and the electrode.

[0017] The method of introducing a multidentate ligand into a binder resin will be explained by way of the following embodiments.

#### Embodiment 1

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[0018] In the first method, a resin into which a desired multidentate ligand was introduced was used as an additive component in the binder resin (a reactive thinner, a hardener, or the like).

[0019] For example, a linear epoxy resin with a molecular chain into which a dicarbonyl group expressed by the chemical formulal below was introduced is mixed with a ring-opening catalyst, which then is applied to the surface of an electrode (Cu foil). When the resin is heated and hardened, the dicarbonyl group in the central part of the molecule forms a coordinate bond with the electrode (Cu foil) expressed by the chemical formula 2 below. Naturally, the epoxy rings at the both ends of the molecule open and form bridge bonds.

## (chemical formula 1)

[0020] The binder resin used here includes as the main component an ordinary epoxy resin without any ligand (bisphenol A, bisphenol F, a novolak epoxy resin). The above resin into which the multidentate ligand was introduced is used by mixing and kneading so as to be contained in the binder resin in an amount between 10 and 50 wt%.

[0021] Furthermore, a ligand can be introduced into a resin to be used as a hardener in the binder resin, not only for the reactive thinner.

#### Embodiment 2

[0022] In the second method, a resin into which a desired multidentate ligand was introduced was used as the main component (the component contained in the largest amount) in the binder resin.

[0023] For example, a bisphenol F-type epoxy resin with a molecular chain into which a dicarbonyl group expressed by the chemical formula 3 below was introduced is mixed with a ring-opening catalyst, which then is applied to the ..., surface of an electrode (Cu foil). When the resin is heated and hardened, the dicarbonyl group in the central part of the molecule forms a coordinate bond with the electrode (Cu foil) as in Embodiment 1.

#### (chemical formula 3)

[0024] The binder resin used here includes as the accessory component an ordinary epoxy resin without any ligand (a reactive thinner, a hardener, or the like). The above resin into which the multidentate ligand was introduced is used by mixing and kneading so as to be contained in the binder resin in an amount between 30 and 100 wt%.

[0025] In the adhesive and the connection structure of the present invention described above, it is preferable that the multidentate bonding is formed in a number between 2 and 4. Naturally, the number of the multidentate bonding may be larger.

[0026] Furthermore, in the adhesive and the connection structure described above, it is preferable that the resin

containing a functional group in its molecular chain that forms a multidentate bonding is present in an amount between 10 and 100 wt% of the total resin.

[0027] Furthermore, in the adhesive and the connection structure described above, it is preferable that, taking the conductive adhesive as 100 wt%, the binder resin is contained in an amount between 5 and 25 wt%, and the metal filler is contained in an amount between 75 and 95wt%. Besides, if necessary, a hardener, a hardening catalyst, a crosslinking agent, and a ring-opening catalyst for the binder resin, a dispersing agent for the metal filler, a viscosity modifier, a pH modifier, or the like may be added optionally. Therefore, in the present invention, "main components" in the "including a binder resin and a metal filler as main components" refers to the constitution in which the binder resin and the metal filler together comprise at least 90wt% of the conductive adhesive.

[0028] Furthermore, in the adhesive and the connection structure described above, it is preferable that at least two 10 functional groups are present, which may be the same or different, selected from the group consisting of a carbonyl group, a carboxyl group, an amino group, an imino group, an iminoacetic acid group, an iminopropionic acid group, a hydroxyl group, a thiol group, a pyridinium group, an imido group, an azo group, a nitrilo group, an ammonium group and an imidazole group.

[0029] Furthermore, in the adhesive and the connection structure described above, it is preferable that the metal filler is at least one particle selected from the group consisting of silver, silver-plated nickel and silver-plated copper. When the surface of the metal filler is silver, it does not react with the ligand of the binder resin but the ligand reacts selectively with the electrode metal. However, when the ligand of the binder resin is contained in a large amount, even if copper is used as the metal filler, for example, since not all the ligands react with the metal filler, copper also can be used as the metal filler.

[0030] Furthermore, in the adhesive and the connection structure described above, it is preferable that the binder resin is at least one resin selected from a thermoplastic resin and a thermosetting resin.

[0031] Furthermore, in the adhesive and the connection structure described above, it is preferable that the thermoplastic resin is at least one resin selected from the group consisting of a polyester resin, a silicone resin, a vinyl resin, a vinyl chloride resin, an acrylic resin, a polystyrene resin, an ionomer resin, a polymethylpentene resin, a polyimide resin, a polycarbonate resin, a fluororesin and a thermoplastic epoxy resin.

[0032] According to the invention described above, the mounting technique by the conductive adhesive with considerably improved adhesive strength can be realized.

[0033] When the conductive adhesive of the present invention and the electrode metal contact each other, the ligand of the binder resin very easily reacts with the metal, so that the ligand is coordinated quickly with the electrode metal to form a chelating ligand, i.e. a strong chemical bonding. Since the ligand is bonded to the molecular chain of the resin, the bonding also is strengthened between the binder resin and the electrode metal as well as between the conductive adhesive and the electrode metal.

[0034] The connection structure of the present invention is formed by electrically connecting the conductive adhesive of the present invention with the electrode, so that this connection structure has improved adhesive strength than conventional connection structures. Moreover, since the thermoplastic resin has excellent flexibility in comparison with a thermosetting resin, this conductive adhesive can achieve a bonding with excellent stress relaxation capability against bending stress.

[0035] The connection structure of the present invention preferably is formed by mounting a component and a substrate by using the conductive adhesive described above, which can improve the adhesive strength against bending stress even more.

[0036] The present invention can be used in place of the conventional solder, for example, as a conductive adhesive to bond a semiconductor substrate with an electronic component chip. Furthermore, the conductive adhesive also can be applied to a conductive paste by filling the conductive adhesive into through holes made in an electrical insulating base material so as to achieve electrical continuity in the thickness direction of the electrical insulating base material. [0037] FIG. 1 is a cross-sectional view showing a mounted structure used for the evaluation of one embodiment of the present invention.

[0038] FIG. 2 is a cross-sectional illustrative view showing the evaluation method of one embodiment of the present invention.

[0039] Hereinafter, the present invention will be described by way of examples with reference to drawings.

## Common experimental method

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[0040] FIG. 1 is a side view of a mounted structure used for the evaluation. A conductive adhesive 3 is screen-printed onto an electrode 2 disposed on a substrate 1, and after an electrode 5 of a component 4 is mounted, the structure is  $heated in an oven \ at \ 150^{\circ}C for \ 30 \ minutes. \ Thus, the mounted structure \ was \ created. \ The \ material \ used for the \ substrate$ 1 and the component 4 was the same, and the material used for the electrode 2 and the electrode 5 was the same. [0041] The evaluation method is shown in FIG. 2. First, pressure was provided to the component 4 from the rear

side of the mounted structure created as above by using a substrate pushing jig 6. The amount of deflection was
measured when the connection resistance had risen to at least twice as much as the initial value. Then, the adhesive
strength against the bending stress was evaluated. The distance between substrate fixing jigs 7 and 8 was determined
to be 100mm.

- [0042] The substrate and the component will be described more in detail.
  - (1) Component: 0 ohmic resistance

base material; alumina or a glass epoxy substrate (3216 size) electrode specification; as shown in Table 1

(2) Substrate

base material; alumina or a glass epoxy substrate (30×150×1.6mm) electrode specification; as shown in Table 1

(3) Conductive adhesive

filler; silver powder (85wt%) (average particle diameter: 3 to 10 μm) binder resin (15wt%); as shown in Table 1

[0043] Hereinafter, the respective embodiments will be explained in detail. In Examples 1 and 2, the conductive adhesive includes a material in which a functional group was introduced into a thermosetting resin. In Examples 3 and 4, the conductive adhesive includes a material in which a functional group was introduced into a thermoplastic resin.

#### Example 1

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[0044] Example 1 is an example, as already explained in Embodiment 1, in which a resin into which a multidentate ligand was introduced was used as an additive component (a reactive thinner).

[0045] The binder resin used for the conductive adhesive was obtained by mixing 15 wt% of a reactive thinner in which a dicarbonyl group expressed by the chemical formula 4 below was introduced into its molecular chain, 75 wt% of a bisphenol F epoxy resin, 5 wt% of a hardener (maleic anhydride), and 5 wt% of a solvent (butyl carbitol acetate).

# (chemical formula 4)

[0046] As a result, in comparison with the cases of Comparative Example 1 (a conventional conductive adhesive), Comparative Example 5 (a silane coupling agent was added), and Comparative Example 7 (an epoxy resin into which a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved.

## 40 Example 2

**[0047]** The binder resin used for the conductive adhesive was the same epoxy resin as in Example 1 in which a dicarbonyl group was bonded to its side chain (chemical formula 4 above). A conventional Cu thick foil was used as the electrode.

[0048] As a result, in comparison with the cases of Comparative Example 2 (a conventional conductive adhesive), Comparative Example 6 (a silane coupling agent was added), and Comparative Example 8 (an epoxy resin into which a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved.

#### Example 3

[0049] Except that a thermoplastic silicone resin was used in which a dicarbonyl group was introduced into the side chain of silicone expressed by the chemical formula 5 below, the constitutions were the same as in Example 1.

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(chemical formula 5) 
$$\begin{array}{c|cccc} C H3 & C H3 \\ HO-S & i-O-S & i-OH \\ HO-C & C-OH \\ \parallel & \parallel \\ O & O \end{array}$$

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[0050] As a result, in comparison with the cases of Comparative Example 1 (a conventional conductive adhesive), Comparative Example 5 (a silane coupling agent was added), and Comparative Example 7 (an epoxy resin into which a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved.

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## Example 4

[0051] The binder resin used for the conductive adhesive was the resin in which a dicarbonyl group was bonded to the side chain of a silicone resin expressed by the chemical formula 4 above. A conventional Cu foil was used as the electrode.

[0052] As a result, in comparison with the cases of Comparative Example 2 (a conventional conductive adhesive), Comparative Example 6 (a silane coupling agent was added), and Comparative Example 8 (an epoxy resin into which a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved. Furthermore, the adhesive strength was higher than in Example 2.

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#### Example 5

[0053] Except that an epoxy resin was used in which the ligand to be introduced into the resin was changed to an aminocarbonyl group in Example 1 expressed by the chemical formula 6 below, the constitutions were the same as in Example 1.

(chemical formula 6)

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$$CH_2-CH-CH_2-O-CH-CH_2-C-O-CH_2-CH-CH_2$$
 $O$ 
 $NH_2$ 
 $O$ 

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[0054] As a result, in comparison with the cases of Comparative Example 1 (a conventional conductive adhesive), Comparative Example 5 (a silane coupling agent was added), and Comparative Example 7 (an epoxy resin into which a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved.

45 Example 6

[0055] Except that the electrode was changed to a calcined Cu thick foil, the constitutions were the same as in Example 5.

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[0056] As a result, in comparison with the cases of Comparative Example 2 (a conventional conductive adhesive), Comparative Example 6 (a silane coupling agent was added), and Comparative Example 8 (an epoxy resin into which a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved.

Example 7

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[0057] Except that an epoxy resin was used in which the ligand to be introduced into the resin was changed to a dicarbonyl group in Example 1 expressed by the chemical formula 7 below, the constitutions were the same as in Example 1.

# (chemical formula 7)

$$CH_2-CH-C-CH_2-C-NH-C-CH_2-C-CH-CH_2$$

[0058] As a result, in comparison with the cases of Comparative Example 1 (a conventional conductive adhesive), Comparative Example 5 (a silane coupling agent was added), and Comparative Example 7 (an epoxy resin into which a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved.

## Example 8

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[0059] Except that the electrode was changed to a calcined Cu thick foil, the constitutions were the same as in Example 7.

[0060] As a result, in comparison with the cases of Comparative Example 2 (a conventional conductive adhesive), Comparative Example 6 (a silane coupling agent was added), and Comparative Example 8 (an epoxy resin into which a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved.

## Example 9

[0061] Except that an epoxy resin was used in which the ligand to be introduced into the resin was changed to a dicarbonyl group expressed by the chemical formula 8 below, the constitutions were the same as in Example 1.

# (chemical formula 8)

[0062] As a result, in comparison with the cases of Comparative Example 1 (a conventional conductive adhesive), Comparative Example 5 (a silane coupling agent was added), and Comparative Example 7 (an epoxy resin into which a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved.

#### Example 10

[0063] Except that the electrode was changed to a calcined Cu thick foil, the constitutions were the same as in Example 9.

[0064] As a result, in comparison with the cases of Comparative Example 2 (a conventional conductive adhesive), Comparative Example 6 (a silane coupling agent was added), and Comparative Example 8 (an epoxy resin into which a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved.

## Example 11

[0065] Except that an epoxy resin was used in which the ligand to be introduced into the resin was changed to a

dicarbonyl group expressed by the chemical formula 9 below, the constitutions were the same as in Example 1.

# (chemical formula 9)

[0066] As a result, in comparison with the cases of Comparative Example 1 (a conventional conductive adhesive), Comparative Example 5 (a silane coupling agent was added), and Comparative Example 7 (an epoxy resin into which a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved.

## Example 12

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[0067] Except that the electrode was changed to a calcined Cu thick foil, the constitutions were the same as in Example 11.

[0068] As a result, in comparison with the cases of Comparative Example 2 (a conventional conductive adhesive), Comparative Example 6 (a silane coupling agent was added), and Comparative Example 8 (an epoxy resin into which a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved.

### Example 13

[0069] Except that an epoxy resin was used in which the ligand to be introduced into the resin was changed to a dicarbonyl group expressed by the chemical formula 10 below (where n indicates a degree of polymerization of about 2 in average), the constitutions were the same as in Example 1.

# (chemical formula 10)

[0070] As a result, in comparison with the cases of Comparative Example 1 (a conventional conductive adhesive), Comparative Example 5 (a silane coupling agent was added), and Comparative Example 7 (an epoxy resin into which

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. a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved.

## Example 14

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[0071] Except that the electrode was changed to a calcined Cu thick foil, the constitutions were the same as in Example 13.

[0072] As a result, in comparison with the cases of Comparative Example 2 (a conventional conductive adhesive), Comparative Example 6 (a silane coupling agent was added), and Comparative Example 8 (an epoxy resin into which a phosphoric ester group was introduced), the amount of deflection at the time of NG rose, and the adhesive strength against the bending stress improved.

## Comparative Example 1

[0073] Except that a conventional conductive adhesive of the following composition was used in place of the binder resin in Example 1, the experiment was performed in the same manner as in Example 1.

- bisphenol F-type epoxy resin 90 wt%
- hardener (diethylenetriamine) 5 wt%
- solvent (butyl carbitol acetate) 5 wt%

## Comparative Example 2

[0074] Except that a calcined Cu thick foil was used in place of the Cu foil in Comparative Example 1, the experiment was performed in the same manner as in Comparative Example 1.

#### Comparative Example 3

[0075] Except that a both-end hydrogen-dimethyl disilicone resin was used in place of the binder resin in Example 30 3, the experiment was performed in the same manner as in Example 1.

#### Comparative Example 4

[0076] Except that a calcined Cu thick foil was used in place of the Cu foil in Comparative Example 3, the experiment was performed in the same manner as in Comparative Example 3.

#### Comparative Example 5

[0077] Except that a silane coupling agent was used in place of the binder resin in Example 1, the experiment was performed in the same manner as in Example 1.

#### Comparative Example 6

[0078] Except that a calcined Cu thick foil was used in place of the Cu foil in Comparative Example 5, the experiment was performed in the same manner as in Comparative Example 5.

#### Comparative Example 7

[0079] Except that an epoxy resin in which a phosphoric ester group was introduced into its molecular skeleton was used in place of the binder resin in Example 1, the experiment was performed in the same manner as in Example 1.

#### Comparative Example 8

[0080] Except that a calcined Cu thick foil was used in place of the Cu foil in Comparative Example 7, the experiment was performed in the same manner as in Comparative Example 7.

[0081] All the results of Examples 1 to 14 and Comparative Examples 1 to 8 above of the present invention are shown in Table 1 below.

Table 1-1

|    | Experimental No.  | Conductive Adhesive          |                                    |  |                     |  |  |
|----|-------------------|------------------------------|------------------------------------|--|---------------------|--|--|
| 5  |                   |                              | Binder Resin                       | Rate of Content (in total resin) (wt%) | Conductive particle |  |  |
|    |                   | Resin introduced with ligand |                                    |  |                     |  |  |
| 10 |                   | Skeleton                     | Ligand                             |  |                     |  |  |
|    | Example 1         | ероху                        | Dicarbonyl group                   | . 15                                   | Ag                  |  |  |
|    | Example 2         | ероху                        | Dicarbonyl group                   | 15                                     | Ag .                |  |  |
| 15 | Example 3         | silicone                     | Dicarbonyl group                   | 15                                     | Ag                  |  |  |
|    | Example 4         | silicone                     | Dicarbonyl group                   | 15                                     | Ag                  |  |  |
|    | Example 5         | ероху                        | Aminocarbon-yl group               | 15                                     | Ag                  |  |  |
|    | Example 6         | ероху                        | Aminocarbon-yl group               | 15                                     | Ag                  |  |  |
| 20 | Example 7         | ероху                        | Dicarbonyl group                   | 15                                     | Ag                  |  |  |
|    | Example 8         | ероху                        | Dicarbonyl group                   | 15                                     | Ag                  |  |  |
|    | Example 9         | ероху                        | Dicarbonyl group                   | 15                                     | Ag                  |  |  |
|    | Example 10        | ероху                        | Dicarbonyl group                   | 15                                     | Ag                  |  |  |
| 25 | Example 11        | ероху                        | Dicarbonyl group                   | 65                                     | Ag                  |  |  |
|    | Example 12        | ероху                        | Dicarbonyl group                   | 65                                     | Ag                  |  |  |
|    | Example 13        | ероху                        | Dicarbonyl group                   | 65                                     | Ag                  |  |  |
|    | Example 14        | ероху                        | Dicarbonyl group                   | 65                                     | Ag                  |  |  |
| 30 | Compar. Example 1 | ероху                        | None                               | 0                                      | Ag                  |  |  |
|    | Compar. Example 2 | ероху                        | None                               | 0                                      | Ag                  |  |  |
|    | Compar. Example 3 | silicone                     | None                               | 0                                      | Ag                  |  |  |
| 35 | Compar. Example 4 | silicone                     | None                               | 0                                      | Ag                  |  |  |
|    | Compar. Example 5 | ероху                        | None (silane coupling agent added) | 0                                      | Ag                  |  |  |
| 40 | Compar. Example 6 | ероху                        | None (silane coupling agent added) | 0                                      | Ag                  |  |  |
|    | Compar. Example 7 | ероху                        | a phosphoric ester group           | 15                                     | Ag                  |  |  |
|    | Compar. Example 8 | ероху                        | a phosphoric ester group           | 15                                     | Ag                  |  |  |

Table 1-2

| Experimental<br>No. |                  | Substrate ar              | Results of Bending Test |                   |  |                              |
|---------------------|------------------|---------------------------|-------------------------|-------------------|--|------------------------------|
|                     | Base<br>Material | Electrode Specification   |                         |                   | Deflection at<br>the time of<br>NG(mm) | Initial<br>Resistance<br>(Ω) |
|                     |                  | Material                  | Porosity<br>(vol%)      | Roughness<br>(μm) |  |                              |
| Example 1           | glass epoxy      | Cu foil                   |                         | 0.1               | 7.5                                    | 0.15                         |
| Example 2           | alumina          | Calcined Cu<br>thick foil | 2.0                     |                   | 9.6                                    | 0.20                         |

Table 1-2 (continued)

|    | Experimental No.     | ,                | Substrate and Component     |                    |                   | Results of Bending Test                |                              |
|----|----------------------|------------------|-----------------------------|--------------------|-------------------|--|------------------------------|
| 5  |                      | Base<br>Material | Electrode Specification     |                    |                   | Deflection at<br>the time of<br>NG(mm) | Initial<br>Resistance<br>(Ω) |
| 10 |                      |                  | Material                    | Porosity<br>(vol%) | Roughness<br>(µm) |  |                              |
| Ĭ  | Example 3            | glass epoxy      | Cu foil                     | _                  | 0.1               | 8.9                                    | 0.20                         |
|    | Example 4            | alumina          | Calcined Cu<br>thick foil   | 2.0                | _                 | 10.7                                   | 0.20                         |
| 5  | Example 5            | glass epoxy      | Cu foil                     | _                  | 0.1               | 7.3                                    | 0.15                         |
|    | Example 6            | alumina          | Calcined Cu<br>thick foil   | 2.0                | _                 | 9.9                                    | 0.18                         |
| Î  | Example 7            | glass epoxy      | Cu foil                     |                    | 0.1               | 7.4                                    | 0.16                         |
| 20 | Example 8            | alumina          | Calcined Cu<br>thick foil   | 2.0                | _                 | 9.8                                    | 0.15                         |
|    | Example 9            | glass epoxy      | Cu foil                     | _                  | 0.1               | 7.6                                    | 0.12                         |
| 25 | Example 10           | alumina          | Calcined Cu<br>thick foil   | 2.0                |                   | 9.9                                    | 0.15                         |
|    | Example 11           | glass epoxy      | Cu foil                     |                    | 0.1               | 7.7                                    | 0.22                         |
|    | Example 12           | alumina          | Calcined Cu<br>thick foil   | 2.0                | _                 | 10.0                                   | 0.20                         |
| 30 | Example 13           | glass epoxy      | Cu foil                     | <del></del>        | 0.1               | 7.8                                    | 0.21                         |
|    | Example 14           | alumina          | Calcined Cu<br>thick foil   | 2.0                |                   | 10.1                                   | 0.19                         |
| 35 | Compar.<br>Example 1 | glass epoxy      | Cu foil                     |                    | 0.1               | 2.4                                    | 0.20                         |
|    | Compar.<br>Example 2 | alumina          | Calcined Cu<br>thick foil . | 2.0                |                   | 2.8                                    | 0.20                         |
| 10 | Compar.<br>Example 3 | glass epoxy      | Cu foil                     | _                  | 0.1               | 0.7                                    | 0.20                         |
|    | Compar.<br>Example 4 | alumina          | Calcined Cu<br>thick foil   | 2.0                | _                 | 0.9                                    | 0.20                         |
| 15 | Compar.<br>Example 5 | glass epoxy      | Cu foil                     | _                  | 0.1               | 3.2                                    | 0.10                         |
|    | Compar.<br>Example 6 | alumina          | Calcined Cu<br>thick foil   | 2.0                | _                 | 3.3                                    | 0.20                         |
| 50 | Compar.<br>Example 7 | glass epoxy      | Cu foil                     |                    | 0.1               | 3.8                                    | 0.20                         |
|    | Compar.<br>Example 8 | alumina          | Calcined Cu<br>thick foil   | 2.0                | _                 | 4.2                                    | 0.20                         |

[0082] In the Examples of the present invention above, the binder resins used for the conductive adhesive were only an epoxy resin and a silicone resin, but other resins described in the Embodiments also are effective for use. Moreover, only a dicarbonyl group was shown as the ligand bonded to the side chain of the binder resin, but other ligands described in the Embodiments also may be used. Furthermore, only copper was used as the electrode metal, but other metals

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generally used for electrodes as described in the Embodiments also may be used.

**[0083]** According to the present invention, the problems with regard to the mounting of conductive adhesives, i.e. the adhesive strength and particularly the strength against the bending stress, can be solved easily. The present invention greatly contributes to the commercial application of the mounting technique using conductive adhesives.

#### Claims

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- 1. A conductive adhesive comprising a binder resin and a metal filler as main components, wherein the binder resin contains a functional group in its molecular chain that forms a multidentate bonding with an electrode metal after the binder resin is adhered and wherein taking the conductive adhesive as 100 wt%, the binder resin is contained in an amount between 5 and 25 wt%, and the metal filler is contained in an amount between 75 and 95 wt%.
- 2. The conductive adhesive according to claim 1, wherein the functional group is capable of forming between 2 and 4 bonds.
  - 3. The conductive adhesive according to claim 1 and/or 2, wherein the resin containing a functional group in its molecular chain is present in an amount between 10 and 100 wt% of the total binder resin.
- 4. The conductive adhesive according to anyone of claims 1 to 3, wherein at least two functional groups are present, which may be the same or different, selected from the group consisting of a carbonyl group, a carboxyl group, an amino group, and imino group, an iminoacetic acid group, an iminopropionic acid group, a hydroxyl group, a thiol group, a pyridinium group, an imido group, an azo group, a nitrilo group, an ammonium group and an imidazole group:
  - 5. The conductive adhesive according to anyone of claims 1 to 4, wherein the metal filler is at least one particle selected from the group consisting of silver, silver-plated nickel and silver-plated copper.
- 6. The conductive adhesive according to anyone of claims 1 to 5, wherein the binder resin is at least one resin selected from a thermoplastic resin and a thermosetting resin.
  - 7. The conductive adhesive according to claim 6, wherein the thermoplastic resin is at least one resin selected from the group consisting of a polyester resin, a silicone resin, a vinyl resin, a vinyl chloride resin, an acrylic resin, a polystyrene resin, an ionomer resin, a polymethylpentene resin, a polyimide resin, a polycarbonate resin, a fluoro resin and a thermoplastic epoxy resin.
  - 8. A connection structure formed by using a conductive adhesive claimed in one of claims 1 to 7 to connect the adhesive with an electrode electrically.
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   9. A method for manufacturing a connection structure formed by using a conductive adhesive claimed in one of claims
   1 to 7 to connect the adhesive with an electrode electrically.

## Patentansprüche

- Leitfähiger Klebstoff, umfassend ein Bindemittelharz und einen Metallfüllstoff als Hauptkomponenten, wobei das Bindemittelharz in seiner Molekülkette eine funktionelle Gruppe enthält, die eine mehrzähnige Bindung mit einem Elektrodenmetall ausbildet, nachdem das Bindemittelharz aufgebracht ist und wobei das Bindemittelharz in einer Menge zwischen 5 und 25 Gew% und der Metallfüllstoff in einer Menge zwischen 75 und 95 Gew% enthalten ist, wenn man den leitfähigen Klebstoff als 100 Gew% nimmt.
- 2. Leitfähiger Klebstoff nach Anspruch 1, worin die funktionelle Gruppe zwischen 2 und 4 Bindungen ausbilden kann.
- Leitfähiger Klebstoff nach Anspruch 1 und/oder 2, worin das eine funktionelle Gruppe in seiner Molekülkette enthaltende Harz in einer Menge zwischen 10 und 100 Gew% des gesamten Bindemittelharzes vorliegt.
- 4. Leitfähiger Klebstoff gemäß jedem der Ansprüche 1 bis 3, worin wenigstens zwei funktionelle Gruppen vorliegen, welche gleich oder verschieden voneinander sind und aus der Gruppe ausgewählt sind, die aus einer Carbonyl-

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gruppe, einer Carboxylgruppe, einer Amingruppe, einer Iminogruppe, einer Iminoessigsäuregruppe, einer Iminopropionsäuregruppe, einer Hydroxylgruppe, einer Thiolgruppe, einer Pyridiniumgruppe, einer Imidogruppe, einer Azogruppe, einer Nitrilgruppe, einer Ammoniumgruppe und einer Imidazolgruppe besteht.

- Leitfähiger Klebstoff gemäß jedem der Ansprüche 1 bis 4, worin der Metallfüllstoff wenigstens ein Partikel ist, das aus der Gruppe ausgewählt ist, die aus Silber, silberplattiertem Nickel und silberplattiertem Kupfer besteht.
  - 6. Leitfähiger Klebstoff nach jedem der Ansprüche 1 bis 5, worin das Bindemittelharz wenigstens ein Harz ist, das aus einem thermoplastischen Harz und einem wärmeaushärtenden Harz ausgewählt ist.
  - 7. Leitfähiger Klebstoff nach Anspruch 6, worin das thermoplastische Harz wenigstens ein Harz ist, das aus der Gruppe ausgewählt ist, die aus einem Polyesterharz, einem Silikonharz, einem Vinylharz, einem Vinylchloridharz, einem Acrylharz, einem Polystyrolharz, einem ionomeren Harz, einem Polymethylpentenharz, einem Polyimidharz, einem Polycarbonatharz, einem Fluorharz und einem thermoplastischen Epoxidharz besteht.
  - 8. Verbindungsstruktur, die unter Verwendung eines in einem der Ansprüche 1 bis 7 beanspruchten leitfähigen Klebstoffes ausgebildet ist, um den Klebstoff mit einer Elektrode elektrische zu verbinden.
- Verfahren zur Herstellung einer Verbindungsstruktur, ausgebildet unter Verwendung eines in einem der Ansprüche
   1 bis 7 beanspruchten Klebstoffes, um den Klebstoff mit einer Elektrode elektrisch zu verbinden.

#### Revendications

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- 1. Un adhésif conducteur comportant une résine liante et un métal d'apport comme composants principaux, dans lequel la résine liante contient un groupe fonctionnel dans sa chaîne moléculaire formant une liaison multivalente avec un métal d'électrode après que la résine liante a été appliquée et dans lequel, en considérant que l'adhésif conducteur représente 100 % en poids, la teneur de la résine liante représente entre 5 % en poids et 25 % en poids, et la teneur du métal d'apport représente entre 75 % en poids et 95 % en poids.
- L'adhésif conducteur selon la revendication 1, dans lequel le groupe fonctionnel est capable de former entre 2 et 4 liaisons.
- 3. L'adhésif conducteur selon la revendication 1 et/ou 2, dans lequel la résine contenant un groupe fonctionnel dans sa chaîne moléculaire représente une quantité entre 10 % et 100 % du total de la résine liante.
  - 4. L'adhésif conducteur selon l'une quelconque des revendications 1 à 3, dans lequel au moins deux groupes fonctionnels sont présents, qui peuvent être les mêmes ou différents, sélectionnés parmi le groupe comprenant un groupe carbonyle, un groupe carboxyle, un groupe amino, un groupe imino, un groupe acide iminoacétique, un groupe acide iminopropionique, un groupe hydroxyle, un groupe mercaptan, un groupe pyridine, un groupe imide, un groupe azoïque, un groupe nitriloacétique, un groupe ammonium et un groupe imidazole.
  - 5. L'adhésif conducteur selon l'une quelconque des revendications 1 à 4, dans lequel le métal d'apport est au moins une particule sélectionnée parmi le groupe comprenant l'argent, le nickel argenté et le cuivre argenté.
  - 6. L'adhésif conducteur selon l'une quelconque des revendications 1 à 5, dans lequel la résine liante est au moins une résine sélectionnée parmi une résine thermoplastique et une résine thermodurcissable.
  - 7. L'adhésif conducteur selon la revendication 6, dans lequel la résine thermoplastique est au moins une résine sélectionnée parmi le groupe comprenant une résine polyester, une résine silicone, une résine vinyle, une résine chlorure de vinyle, une résine acrylique, une résine polystyrène, une résine ionomère, une résine polyméthylpentène, une résine polyimide, une résine de polycarbonate, une résine fluorocarbonée et une résine époxy thermoplastique.
- 8. Une structure de connexion formée en utilisant un adhésif conducteur selon l'une des revendications 1 à 7 pour connecter électriquement l'adhésif à une électrode
  - 9. Une méthode pour la fabrication d'une structure de connexion formée en utilisant un adhésif conducteur selon

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l'une des revendications 1 à 7 pour connecter électriquement l'adhésif à une électrode.

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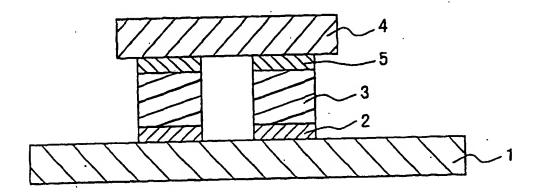


FIG.1

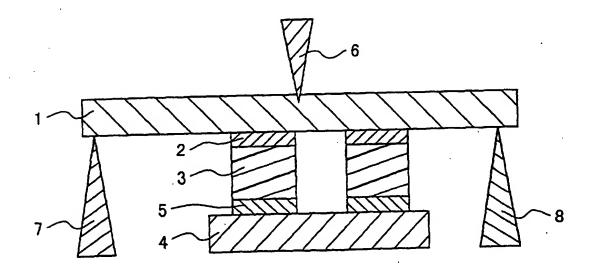


FIG . 2

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